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ON THE DETERMINATION OF PHOSPHORIC ACID IN SOILS.

A Reply to Professor Booth's Article on the Practical Value of the Analysis of Soils. By CHAS. BICKELL, Assistant State Chemist of Maryland. Read before the Baltimore Academy of Science and Arts, November 2, 1893.

THE National Intelligencer of the 20th of August last contains an article, just read before you, on the Practical Value of the Analysis of Soils, by JAMES E. BOOTH, the well-known Professor of Philadelphia, in which the practical worthlessness of the analysis of soils is sought to be shown; or, in other words, in which a structure is sought to be destroyed that science has for more than twenty years resolutely endeavored to erect, and the strong and durable foundation of which is sustained not only by the experience of a Berzelius, Liebig, Rose, Way, and others, but also by the fact that we take the trouble of investigating the subject.

The relation between the physiology of plants and their culture, in its practical use and importance to the farmer, is, according to Prof. Booth, totally destroyed; for, although we are enabled to indicate with certainty the substances and their quantity which a crop extracts from the soil, we are nevertheless unable to know whether a soil contains these parts, and whether their quantity is sufficient to produce another crop. This is the assertion of Prof. Booth, which he pronounces indirectly in the three ensuing sections of his article:

1. It is impossible to procure a fair average of a soil for examination.
2. Suppose a fair sample could be obtained, then the present advancement of science is not such as to enable the making of a correct analysis.
3. Suppose an analysis could be made, then the expenses connected with it would be so enormous that it would be of no practical value to the farmer.

At the end of a very hasty and imperfect argument to demonstrate the truth of these assertions, Prof. Booth finally expresses the sweet hope that the time would come when analytical chemistry would be, in its continual improvement, so far progressed that experiments of this sort may be made with satisfactory correctness, and when we shall find the verification of this sentiment:

"The desert shall blossom as the rose."

Even if we suppose Prof. Booth's opinion to be established as a sad truth, we cannot refrain from recognizing in the philosophy of the words, so boldly pronounced by him, nothing but the effusion of a mind which has been, in the multiplicity of its investigations, but little directed to the subject on which he writes. We need not to be told that our knowledge is far from being perfect, and that we must strive for perfection; we are all aware that this refers to all our actions. It is undoubtedly a more advisable and better occupation for our mind to dwell on much profit as possible out of what we have established as truth, and apply it to the advantage of the present time; or, in opening a new field of observations and exploring it, we are compelled to apprise the world indirectly that we have been wrapped up heretofore in error.

Prof. Booth proceeds on another principle. In the above-mentioned article, which is a transcript of his address to the Philadelphia Society for the Promotion of Agriculture, he depicts the present condition of analytical chemistry in the most deplorable manner, and comes finally to the conclusion that both our methods of analysis and our balances must be perfected before we can think of a satisfactory result. He says: "The present condition of analytical chemistry is such that it is impossible to procure a fair average of a soil for examination, and that the expenses connected with it would be so enormous that it would be of no practical value to the farmer." This solution leaves Prof. Booth to time, which in all probability will greatly postpone his future plans. With regard to a greater refinement or perfection of the balances at present in use, Mr. Jones, as well as any one else acquainted with mechanism, will be able to designate the limit of this perfection, and we are sure that we have already reached that limit. This limit lies in the nature of the thing itself, viz. that the sensibility of a balance increases with the length of the beam and decreases in proportion to the weight of the beam.

If we were to apply long beams, we would, in accordance with this principle, find that they must lose, on account of their necessary length, their equality, and consequently, not to say aught of their impracticability for common use.

The future consequently does not promise us many remedies in this respect, and Prof. Booth would, sooner or later, and himself disappointed in his hopes, either he might have placed them on steam, electric or magnetic balances, yet to be constructed.

In the same manner resources to the performances of chemical analysis are sought, as we are here advised to depend on the nature of substances. If we lie in the nature of a substance, e. g. of potash, to form characteristic precipitates only with a few substances, (called reagents), which are not even distinguished by their great solubility, neither can we expect that any one man is able to give to the potash other qualities, for potash with other qualities ceases to be potash.

Prof. Booth should not expect too much from the future. It would be much better for him, especially in this matter, to cling to what the moment offers, as it answers the necessity of the purpose which we require. Here, now, I return to the point from which I digressed and which I have made the object of my discussion; that is, the practical refutation of Prof. Booth's assertions. It would carry me too far if I were to comment upon every sentence of his article, and would also become uninteresting to the audience, or a portion of it.

I have the intention to express my views with regard to the analysis of soils from time to time before this assembly, and I shall do so, beginning at the earliest opportunity, in as suitable and concise a manner as possible. To-night I will confine myself to treat upon the analytical determination of a substance in soils, which is decided by Prof. Booth as impracticable, viz. the determination of phosphoric acid. Prof. Booth says as follows about it:

"There is a confirmatory argument against the practical value of soil-analysis, which has been so clearly set up by Major J. F. Lewis, that I take the liberty of quoting his letter to me on the subject:

"We know that on all poor land of proper texture the application of 200 lbs. of guano to the acre will produce a crop of grain and roots. And this is the difference between a barren and a tolerably fertile soil. Now, this guano applies only 4 lbs. of potash, 24 lbs. of phosphoric acid, and 34 lbs. of ammonia. But the soil contains 3,200,000 lbs. of potash, 1,400,000 lbs. of phosphoric acid, and 1,400,000 lbs. of ammonia. It may be reasonably expected that to make, ascertain one part of potash in 600,000 parts of foreign matter, or one part of phosphoric acid in 100,000 parts of foreign matter, or one part of ammonia in 100,000 parts."

It may be answered, without the slightest fear of contradiction, that such determinations are greatly beyond the present power of chemical analysis. Whether they are or not, I shall presently inquire; but the argument is strong against the present value of analysis applied to soils."

These numbers are truly enormous, and every farmer, every man of common education, will be obliged, in perusing the above, to concur with Prof. Booth's difficulties, and to say that the numbers are so large that they are beyond the power of the present power of chemical analysis. But the argument is strong against the present value of analysis applied to soils."

The numbers, as mentioned by Prof. Booth, however great they may appear at first sight, are but fragments of numbers as they are constantly applied in the daily life of chemists; for the chemist is accustomed to precipitate and to recognize even one-millionth part of oxide of barium in solution by means of sulphuric acid, or by means of silver yet one-millionth of hydro-chloric acid, by hydro-chloric acid yet one-millionth of bromine, by oxalic acid 1-100,000th of lime, &c.

Most of the numerous other reagents, commonly applied, indicate even 1-50,000th, 1-100,000th, and yet they are applied. With regard to the above-mentioned phosphoric acid, chemists have been, quite contrary to the assertions of Prof. Booth, very successful in finding reagents which lead to the detection of even the smallest quantity of phosphoric acid, mixed with the most varied foreign matters.

Of the different methods applied to the present day, however accurate and satisfactory they all have proved to be, that which Svaneberg and Struve have first proposed, and by which phosphoric acid is detected by the formation of a yellow color, is the most delicate and the most accurate for the application on soils, furnishing indisputably the most exact results of all, and requiring, besides, little skill, the least time. Not mentioning others, I remark, therefore, exclusively to the latter most important method, which I will lay in the most minute details before the society, guided solely and alone by observations made in a practical manner, in common with Dr. Higgins, in the Laboratory of the State of Maryland.

As at first, to the preparation of the molybdate of ammonia, it is most commonly made from the natural sulphate of molybdenum. This is to be pulverized, or, on account of its toughness, ground to powder, and then to be exposed to the heat and constantly stirred; sulphuric acid with a little nitric acid is then added, and the heat must be moderate, most especially towards the end of the process. The residue is digested for some time with ammonia, which dissolves the molybdic acid,

whilst undecomposed sulphate of molybdenum, quartz, and other substances remain. The filtrate evaporated, and, if necessary, once more distilled, when boiled and mixed, when yet hot, with strong ammonia, will, by cooling, leave crystals of molybdate of ammonia.

A concentrated solution of these crystals in water furnishes the above-mentioned reagent. The effect of the molybdate of ammonia on phosphoric acid and its salts in a solution which has been acidified by nitric acid manifests itself first in the forming of a white precipitate of molybdic acid, which is redissolved, however, in the excess of nitric acid present. The liquid then assumes a yellow color and deposits a yellow precipitate of a crystalline structure, the formation of which is accelerated by heating.

This precipitate consists of about three percent. of phosphoric acid, a very small quantity of ammonia, and, taking the whole rest, of molybdic acid, which are united to each other in a manner yet doubtful. It is easily soluble in ammonia and an excess of phosphates; insoluble, however, in hydrochloric or nitric acid.

These conditions demonstrate at once that the application of this method is especially appropriated to the tracing of small quantities of phosphoric acid, as in soils. In this case no excess of phosphates, in which the formed precipitate could be dissolved, is to be feared, nor the danger to overlook a precipitate, which consists in its whole quantity of substances used for precipitation, with a small portion of the substance which is the object in search.

Direct experiments to test the sensibility of this reagent were made, and the following results obtained: By dissolving 5 grammes of crystallized phosphate of soda, which contain 1 gramme of phosphoric acid, in 25 grammes of water, a solution was obtained which weighed 1-200th, 1-500th, 1-1,000th, 1-2,000th, 1-4,000th, 1-8,000th, 1-16,000th, 1-32,000th, 1-64,000th, 1-128,000th, 1-256,000th, 1-512,000th, 1-1,024,000th, 1-2,048,000th, 1-4,096,000th, 1-8,192,000th, 1-16,384,000th, 1-32,768,000th, 1-65,536,000th, 1-131,072,000th, 1-262,144,000th, 1-524,288,000th, 1-1,048,576,000th, 1-2,097,152,000th, 1-4,194,304,000th, 1-8,388,608,000th, 1-16,777,216,000th, 1-33,554,432,000th, 1-67,108,864,000th, 1-134,217,728,000th, 1-268,435,456,000th, 1-536,870,912,000th, 1-1,073,741,824,000th, 1-2,147,483,648,000th, 1-4,294,967,296,000th, 1-8,589,934,592,000th, 1-17,179,869,184,000th, 1-34,359,738,368,000th, 1-68,719,476,736,000th, 1-137,438,953,472,000th, 1-274,877,906,944,000th, 1-549,755,813,888,000th, 1-1,099,511,627,776,000th, 1-2,199,023,255,552,000th, 1-4,398,046,511,104,000th, 1-8,796,093,022,208,000th, 1-17,592,186,044,416,000th, 1-35,184,372,088,832,000th, 1-70,368,744,177,664,000th, 1-140,737,488,355,328,000th, 1-281,474,976,710,656,000th, 1-562,949,953,421,312,000th, 1-1,125,899,906,842,624,000th, 1-2,251,799,813,685,248,000th, 1-4,503,599,627,370,496,000th, 1-9,007,199,254,740,992,000th, 1-18,014,398,509,481,984,000th, 1-36,028,797,018,963,968,000th, 1-72,057,594,037,927,936,000th, 1-144,115,188,075,855,872,000th, 1-288,230,376,151,711,744,000th, 1-576,460,752,303,423,488,000th, 1-1,152,921,504,606,846,976,000th, 1-2,305,843,009,213,693,952,000th, 1-4,611,686,018,427,387,904,000th, 1-9,223,372,036,854,775,808,000th, 1-18,446,744,073,709,551,616,000th, 1-36,893,488,147,419,103,232,000th, 1-73,786,976,294,838,206,464,000th, 1-147,573,952,589,676,412,928,000th, 1-295,147,905,179,352,825,856,000th, 1-590,295,810,358,705,651,712,000th, 1-1,180,591,620,717,411,303,424,000th, 1-2,361,183,241,434,822,606,848,000th, 1-4,722,366,482,869,645,213,696,000th, 1-9,444,732,965,739,290,427,392,000th, 1-18,889,465,931,478,580,854,784,000th, 1-37,778,931,862,957,161,709,568,000th, 1-75,557,863,725,914,323,419,136,000th, 1-151,115,727,451,828,646,838,272,000th, 1-302,231,454,903,657,293,677,544,000th, 1-604,462,909,807,314,587,355,088,000th, 1-1,208,925,819,614,629,174,710,176,000th, 1-2,417,851,639,229,258,349,420,352,000th, 1-4,835,703,278,458,516,698,840,704,000th, 1-9,671,406,556,917,033,397,681,408,000th, 1-19,342,813,113,834,066,795,362,816,000th, 1-38,685,626,227,668,133,590,725,632,000th, 1-77,371,252,455,336,267,181,451,264,000th, 1-154,742,504,910,672,534,362,902,528,000th, 1-309,485,009,821,345,068,724,705,056,000th, 1-618,970,019,642,690,137,449,410,112,000th, 1-1,237,940,039,285,380,274,898,820,224,000th, 1-2,475,880,078,570,760,549,797,640,448,000th, 1-4,951,760,157,141,521,099,595,280,896,000th, 1-9,903,520,314,283,042,199,190,561,792,000th, 1-19,807,040,628,566,084,398,381,123,584,000th, 1-39,614,081,257,132,168,796,762,247,168,000th, 1-79,228,162,514,264,337,593,524,494,336,000th, 1-158,456,325,028,528,675,187,048,988,672,000th, 1-316,912,650,057,057,350,374,377,977,344,000th, 1-633,825,300,114,114,700,748,755,954,688,000th, 1-1,267,650,600,228,229,401,497,511,909,317,376,000th, 1-2,535,301,200,456,458,802,995,023,818,732,000th, 1-5,070,602,400,912,917,605,990,047,637,464,000th, 1-10,141,204,801,825,835,211,980,095,274,928,000th, 1-20,282,409,603,651,670,423,960,190,549,856,000th, 1-40,564,819,207,303,340,847,920,381,099,712,000th, 1-81,129,638,414,606,681,695,840,762,199,424,000th, 1-162,259,276,829,213,363,391,681,524,398,848,000th, 1-324,518,553,658,426,726,783,363,048,797,696,000th, 1-649,037,107,316,853,453,567,726,097,595,392,000th, 1-1,298,074,214,633,706,907,135,453,451,190,784,000th, 1-2,596,148,429,267,413,814,270,906,902,381,568,000th, 1-5,192,296,858,534,827,628,541,813,804,763,136,000th, 1-10,384,593,717,069,655,257,083,627,609,526,272,000th, 1-20,769,177,434,139,310,514,167,255,255,252,544,000th, 1-41,538,354,868,278,621,028,334,510,510,505,088,000th, 1-83,076,709,736,557,242,056,669,021,021,010,112,000th, 1-166,153,419,473,114,484,113,338,042,042,020,224,000th, 1-332,306,838,946,228,968,226,676,084,084,040,448,000th, 1-664,613,677,892,457,936,453,352,168,168,080,896,000th, 1-1,329,227,355,784,915,872,906,704,336,336,161,792,000th, 1-2,658,454,711,569,831,745,813,408,672,672,384,000th, 1-5,316,909,423,139,663,491,626,816,145,344,768,000th, 1-10,633,818,846,279,326,983,253,632,290,688,153,600th, 1-21,267,637,692,558,653,966,507,264,581,377,307,200th, 1-42,535,275,385,117,307,933,014,528,116,754,614,414,400th, 1-85,070,550,770,234,615,866,028,056,233,508,828,800th, 1-170,141,101,540,469,231,732,112,012,467,017,637,657,600th, 1-340,282,203,080,938,463,464,224,024,934,035,275,315,200th, 1-680,564,406,161,876,926,928,448,048,868,070,550,630,400th, 1-1,361,128,812,323,753,853,856,896,097,737,141,101,260,800th, 1-2,722,257,624,647,507,707,713,792,195,472,282,202,521,600th, 1-5,444,515,249,295,015,415,427,584,390,944,564,405,042,000th, 1-10,889,030,498,590,030,830,855,168,781,888,112,804,084,000th, 1-21,778,060,997,180,061,661,710,336,163,776,225,608,160,000th, 1-43,556,131,994,360,122,322,420,672,327,552,451,216,320,000th, 1-87,112,263,988,720,244,644,841,344,655,104,432,640,640,000th, 1-174,224,527,977,440,489,289,682,688,130,868,880,864,128,000th, 1-348,449,055,954,880,978,578,365,376,261,737,761,728,256,000th, 1-696,898,111,909,761,957,156,730,742,523,475,523,452,512,000th, 1-1,393,796,223,819,523,914,313,461,485,046,946,045,905,024,000th, 1-2,787,592,447,639,047,828,626,922,970,970,890,810,048,000th, 1-5,575,184,895,278,095,657,253,845,941,941,781,620,160,000th, 1-11,150,369,790,556,191,314,507,691,883,883,563,240,320,000th, 1-22,300,739,581,112,382,628,014,767,767,726,480,640,640,000th, 1-44,601,479,162,224,765,256,029,535,535,452,960,128,128,000th, 1-89,202,958,324,449,530,512,059,071,071,905,920,256,256,000th, 1-178,405,916,648,899,061,024,118,142,142,181,840,512,512,000th, 1-356,811,833,297,798,122,048,236,284,284,363,680,102,404,800th, 1-713,623,666,595,596,244,096,472,568,568,727,360,204,808,000th, 1-1,427,247,333,191,192,488,144,113,616,113,454,720,409,616,000th, 1-2,854,494,666,382,384,976,288,227,227,908,840,819,232,000th, 1-5,708,989,332,764,769,952,576,454,454,817,680,163,664,000th, 1-11,417,978,665,529,539,904,115,308,115,235,368,327,328,000th, 1-22,835,957,331,059,079,808,230,616,230,470,736,654,656,000th, 1-45,671,914,662,118,159,616,461,232,461,941,408,130,130,000th, 1-91,343,829,324,236,318,232,922,464,922,882,816,260,260,000th, 1-182,687,658,648,472,636,464,944,944,764,768,520,520,000th, 1-365,375,317,296,945,272,928,888,888,152,888,040,104,000th, 1-730,750,634,593,890,545,856,177,776,177,764,304,304,000th, 1-1,461,501,269,187,781,091,712,355,552,355,528,608,608,000th, 1-2,923,002,538,375,562,182,424,711,104,711,216,121,616,000th, 1-5,846,005,076,751,124,364,848,142,208,142,423,232,232,000th, 1-11,692,010,153,502,248,728,736,284,416,284,846,464,464,000th, 1-23,384,020,307,004,497,456,468,568,568,728,728,928,928,000th, 1-46,768,040,614,008,994,912,937,136,937,456,456,856,856,000th, 1-93,536,081,228,017,989,824,183,272,183,712,712,171,712,000th, 1-187,072,162,456,035,979,648,366,544,366,424,424,343,424,000th, 1-374,144,324,912,071,959,296,733,088,733,848,733,686,848,000th, 1-748,288,649,824,143,918,592,466,176,466,696,696,137,696,000th, 1-1,496,577,299,648,287,837,184,932,352,932,139,352,275,352,000th, 1-2,993,154,599,296,575,674,368,184,368,276,368,550,550,550,000th, 1-5,986,309,198,593,151,348,736,376,736,552,552,110,552,110,000th, 1-11,972,618,397,186,302,696,152,147,147,110,147,220,220,220,000th, 1-23,945,236,794,372,605,392,304,294,294,220,294,440,440,000th, 1-47,890,473,588,745,210,784,608,588,588,440,588,880,880,000th, 1-95,780,947,177,490,421,568,117,117,880,117,776,117,154,154,000th, 1-191,561,894,354,980,843,136,234,234,776,234,668,234,308,308,000th, 1-383,123,788,709,961,686,272,468,468,154,468,336,336,616,616,000th, 1-766,247,577,419,923,372,536,936,936,308,936,672,672,123,672,000th, 1-1,532,495,154,839,846,744,107,107,672,107,344,107,172,172,000th, 1-3,064,990,309,679,693,488,214,214,344,214,688,214,344,344,000th, 1-6,129,980,619,359,386,976,428,428,688,428,136,428,272,272,000th, 1-12,259,961,238,718,773,952,856,856,272,856,544,544,544,000th, 1-24,519,922,477,437,547,904,171,171,544,171,272,171,136,136,000th, 1-49,039,844,954,875,095,808,342,342,108,342,214,342,428,428,000th, 1-98,079,689,909,750,191,616,684,684,216,684,428,428,856,856,000th, 1-196,159,379,819,500,383,232,136,136,428,136,214,136,108,108,000th, 1-392,318,759,639,000,766,464,272,272,856,272,544,272,108,108,000th, 1-784,637,519,278,001,532,928,544,544,108,544,108,216,216,000th, 1-1,569,275,038,556,002,064,105,105,108,105,216,105,432,432,000th, 1-3,138,550,077,112,004,128,210,210,216,210,432,432,864,864,000th, 1-6,277,100,154,224,008,256,420,420,432,420,864,864,172,172,000th, 1-12,554,200,308,448,016,512,840,840,864,840,172,840,344,344,000th, 1-25,108,401,616,896,032,1024,168,168,172,168,344,168,688,688,000th, 1-50,216,803,233,792,064,2048,336,336,344,336,688,688,136,136,000th, 1-100,433,606,467,584,128,4096,672,672,688,672,136,672,272,272,000th, 1-200,867,212,935